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Solid Surface Enhancement Effects on Chemiluminescence. III. Diaryloxalate as Chemiluminescence Reagent and Inorganic Materials as Media Solids

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Solid surface enhancement effects on chemiluminescence were studied using many inorganic materials as solid media. The results has been classified as follows: the first group (G-1) which has higher initial intensities and shorter lifetimes compared with the reference chemiluminescence (blank CL; medium solid used is a slide glass)—Al_2O_3 series including hydroxides and glass fiber filter fall under this group (G-1); the second group (G-2) which has lower initial intensities and longer lifetimes compared with the blank CL—high purity $CaCO_3$ fall under this group (G-2); the third group (G-3) which has higher initial intensities and longer lifetimes compared with the blank CL—SiO_2 powder and a silica fiber filter fall under this group (G-3); and the fourth group (G-4) which has lower initial intensities and shorter lifetimes compared with the blank CL—all remaining solid media other than group (G-1)–(G-3) fall under this group (G-4). Furthermore, from a chemiluminescent energy point of view, there exists another group (G-5) which has higher relative luminescent energies or relative quantum yields than the blank one–all the compounds that belong to the group (G-3) and others in group (G-1) and group (G-2), i.e., silica powder (SW-CO type), silica fiber filter (QR-100 type), and high purity calcium carbonate (3N-D type) are members of this group (G-5). Effects of surface condition and particle size on chemiluminescence were also examined.

Chemiluminescence has been used in many fields, including measurements of the degree of deterioration of polymer compounds[1,2], application to food industries (e.g., to measure the degree of oxidation and deterioration of food oils and fats)[3,4], criminal identification and forensic analysis[5,6], and analytical science fields—detectors for high performance liquid chromatography (HPLC). It is also used for determinations of ozone in air, small amounts of metals in the environment, amines, amino acids, peptides, proteins, enzymes, nucleic acids, organic acids, sugars, cholesterol, urine, and other compounds in the fields of medical science, pharmacy (pharmacology), biochemistry, biology and agriculture[7–16]. Furthermore, in recent years, more daily life applications such as road signs and lighting at night, night fishing, lighting in deep water, and interior lighting have become common.[17,18] We have studied chemiluminescent properties on solid surfaces using diaryloxalate (as a representative of chemiluminescent reagents) and many kinds of solid media which might be used as solid surface enhancers or solid media with interesting characteristics, since we had found interesting solid surface enhancement phenomena. At first, we used varieties of filters as solid media. We found that a certain filter gave interesting chemiluminescent characteristics, and that a glass fiber filter gave the highest intensity enhancement effect among them.[17] Then, standard cellulose fiber filter-paper and cellulose powder (tightly packed) were examined to study the effects of surface states. Next, differences of film state and powder state of synthetic polymers (PVC [poly(vinyl chloride)], and PVA [poly(vinyl alcohol)]) were investigated to determine whether or not they gave different chemiluminescent effects.[18] Effects of functional groups [chemical structures] in cellulose derivatives (chitin, chitosan, acetylcellulose etc.) were also studied,[18] and many other organic polymers including oligomers were also examined. As shown in a previous paper,[17] glass fiber filters and silica fiber filters (inorganic materials) were found to exhibit interesting properties on solid surface chemiluminescence. That is the reason why, in the present work, a number of inorganic compounds and related materials were examined to find new and interesting solid media that show characteristic properties such as solid surface enhancement phenomena.

Experimental

Reagents. **(a) Humidity Regulators.** Saturated aqueous solutions of KOH, $LiCl{\cdot}H_2O$, $CaCl_2{\cdot}6H_2O$, $K_2CO_3{\cdot}2H_2O$,

$Mg(NO_3)_2 \cdot 6H_2O$, NaCl, and $K_2Cr_2O_7$ were prepared in order to regulate the humidity of the sample box to an appropriate value in a double jacket type thermostat made of acrylic resin plates.[17]

(b) Chemiluminescent Reagent. Sticks of chemiluminescent (CL) reagent having the same composition as Cyalume (American Cyanamid Company) were commercially obtained from Nippon Kagaku Hakko Co. Ltd. The constituents of the CL reagent in the stick are described elsewhere.[17]

Solid Media. Around thirty kinds of inorganic compounds and materials [powder, crystal, pellet, fiber, or plate forms] used for chemiluminescent investigations were obtained from the respective manufacturers in Japan. The number of samples examined was about ninety, including the different particle sizes and different treated conditions. Grain sizes of powder samples were adjusted to be 50–74 μm using JIS (Japanese Industrial Standards) 200 mesh (74 μm) and 300 mesh (50 μm) sieves. If samples were pellets or large particles, they were ground to fine particles using a Shibata personal mill (SCM-40A) and particle sizes were adjusted to the same size as stated above. However, if samples obtained had particle sizes smaller than 50 μm (300 mesh), they were used as they were: such as AX-25 (average diameter: 25 μm), and high purity super fine magnesia (100A [= 10 nm], 500A [= 50 nm], and 1000A [= 100 nm]). Solid media are classified into (A)–(E) as follows.

(A) Oxides, Hydroxides and Their Treated Material: Silica(SiO_2) [S-COL, S-CO, S-O, SW-CO] (Maikuron Co. Ltd.), aluminum oxide [012-01965] (Wako Pure Chemical Co. Ltd.), alumina spherical particles [AX-25, AX-50] (Maikuron Co. Ltd.), ultra pure alumina [AKP-30, AKP-50] (Nippon Tokushu Togyo Co. Ltd.), easily sintering alumina [AES-11, AES-12], (low sodium) alumina (Al_2O_3: 99.9%) [AL-41, ALM-41-01], aluminum hydroxides [C-31, C-315, C301, C308, CW-375HT, CW-325LV] (Sumitomo Chemical Industry Co. Ltd.), spherical titanium dioxide [0510, 0511, 1010] (Nippon Soda Co. Ltd.), high purity super fine magnesia [100A, 500A, 1000A, 2000A] (Ube Kosan Co. Ltd.), super fine zinc oxide [ZnO] (Mitsubishi Material Co. Ltd.), high purity zirconia [3Y, 3YB, 3YSB, 3Y20A, 3Y20AB] (Toso Co. Ltd.), high purity mullites ($3Al_2O_3 \cdot 2SiO_2$) [MP-40], and ($3Al_2O_3 \cdot 2SiO_2$-ZrO_2 [15%(w/w)]) (Saimarekku Co. Ltd.) were supplied free of charge by each company.

(A′) Functional Super Fine Powder (In, Sb, Sn, Fe, and Ti related metal oxides super fine particles)**:** (Sb/SnO_2) [T-1], (Sn/In_2O_3) [ITO], white electroconductive hybrid powder ($Sb \cdot SnO_2/TiO_2$) [W-1, W-1-P, W-10], Titanium black ($TiO_{2-\alpha}$) [10-S, 12-S, 13-M, 13-R, 20-M], transparent iron oxide (α-FeOOH) [TY-220, TR-420] (Mitsubishi Material Co. Ltd.)

(B) Non Oxides (chlorides, nitrates, sulfates, sulfides, carbonate, etc.)**:** Only calcium carbonate was used in this work. Ultra pure calcium carbonate samples [3N-A ($<$ 0.5 μm), 3N-B (0.5–1 μm), 3N-C (1–5 μm), 3N-D ($>$ 5 μm): 3N means 99.9%] (Nippon Calceed Co. Ltd.) were supplied free of charge.

(C) Metal Powder: Flat type amorphous metal powder; soft magnetism material, (Co, Fe) SiB, anti-corrosive material (Fe, Ni) (Cr, Mo) PC (Imperial piston ring Co. Ltd.), Copper micro powder (Mitsubishi Gas Chemistry Co. Ltd.) were supplied free of charge by each company.

(D) Ceramics: Hexagonal boron nitride (BN) [GP, SP-1, SP-2] (Denki Kagaku), Metal boride, [TiB2-PF, ZrB2-F, CrB, CrB_2] (Nippon Shinkinzoku), Silicon nitride–silicon carbide complex powder ($Si_3N_4 \cdot SiC$ [30%(w/w)]) (Mitsubishi Gas Chemistry, Co. Ltd.), Silicon nitride powder (α-Si_3N_4(trigonal), β-Si_3N_4 (hexagonal)) [SN-7, SN-9FW, SN-G2, SN-P21C, SH-3MF, SH-3BF, SH-5MF: most samples have more than 90% of α conversion degree, except SN-7 (72%(w/w))] (Onoda Cement Co. Ltd.), Copper coated molybdenum disulfide (Cu-coated MoS_2 [Cu 50%(w/w)]) (Nihon Kogyo Co. Ltd.), Transparent aluminum nitride (AlN) (Tokuyama Soda Co. Ltd.), High temperature type proton electroconductive ceramics ($SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$, $CaZr_{0.9}In_{0.1}O_{3-\alpha}$) (TYK Institute), Stabilized zirconia (ZrO_2-(8 mol%)Y_2O_3) (Fujikura Densen Co. Ltd.), Hyper high strengthened zirconia (Toso Co. Ltd.), Potassium hexatitanate whisker ($K_2O \cdot 6TiO_2$) [Tofica-Y, Tofica-YN] (Nippon whisker), Electroconductive whisker ($K_2O \cdot TiO_2$) [BK-200, BK-300, WK-200, WK-200B, WK-300] (Ohtsuka Kagaku Co. Ltd.) were supplied free of charge by each company.

(E) Others: *Pitch-type carbon fiber* [A-10, A-15, A-20] (Osaka Gas Co. Ltd.), Isotropic carbon [KS, KH] (Kureha Kagaku Industry Co. Ltd.), Carbon micro beads(surface modified micro sphere carbon) [ICB-1020, ICB-2020, ICB-50020, PC-1020, PC-2020, MC-1020] (Nippon Carbon Co. Ltd.) were supplied free of charge by each company.

Filters: (a) Glass fiber filter [GC-50] and (b) Silica fiber filter [QR-100] (Advantech Toyo Co. Ltd.) were obtained commercially.

Apparatus: The intensity of the chemiluminescence was measured with a Sanwa Model SLP-4000 light power meter.[17] The light sensor of the power meter is made from a silicon photodiode. The luminescent intensities ranged from 10 nW to 10 mW. The luminescent intensities were measured in a logarithmic scale (*N*) using a light power meter, but they are easily converted to mW scale (I) using the following formula:

$$N = \log_{10} (I/\text{mW}) \ (= 0.434 \log_e (I/\text{mW})) \tag{1}$$

$$I = 10^N \tag{1$'$}$$

The temperature was regulated using a Taitec CL-80 digital thermostat by circulating water of constant temperature through a measuring box which was composed of double jackets made of transparent acrylic resin plates.[18]

Measurement: The experimental procedures for the measurement of chemiluminescence were the same as those reported previously.[17,18] They will be explained here briefly. The CL capsule is composed of two tubes (an inner glass tube [H_2O_2] and an outer polyethylene tube [CL reagent and related compounds]). The CL reagent contained in a capsule is stirred for 10 min. at constant temperature; immediately after it is taken out of the bath, the glass tube in the capsule is broken ($t_1 = 0$ sec) and the reagent is shaken for ten seconds. Then, the capsule tip is cut down and a volume of 100 μL CL reagent is extracted using a micro-syringe and is dropped onto the center of the solid medium. The apparent intensities of chemiluminescence were measured at appropriate intervals (e.g. $t_1 = 60$ sec [$t_2 = 30$ sec], 90 sec, 2 min, 3 min, 5 min, 20 min and so on)[18] until the intensity value with logarithmic scale N (= $\log_{10}$ [I/mW]) decreases to -5.00. In the present work, the influence of thickness of packed powder on chemiluminescence was also examined, and those thicknesses were adjusted using the combination of aluminum plates, which are conventionally used for X-ray diffractometry measurements, and polymer sheets (PVC) with the same forms as aluminum plates, in the range of 0.75 mm to 3.0 mm. Schematic figures of the measurement devices on solid surface chemiluminescence are shown in Fig. 1a [for blank experiment] and 1b [for sample experiment]. Using these experimental data, we have estimated the relative luminescent intensities, lifetimes, and energies (corresponding to

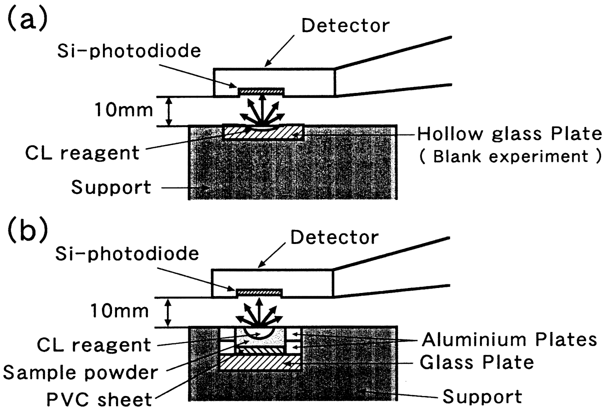


Fig. 1. Schematic drawing for CL measurement devices.

relative quantum yields) to blank luminescence for comparison.

Surface Treatments: In some cases, filter materials that showed interesting luminescent properties were treated using organic solvents (methanol, ethanol, or acetone) or acid (1 M HCl) or base (1 M NaOH). That is, to examine the difference of surface conditions or surface treatment effects of the filter materials, they were dipped into the respective organic solvent, acid or alkaline solution in 200 mL beakers and were shaken for 10 min, then washed in distilled water three times (ca. 10 mL each) and dried for 30 min at 110 °C.

Mechanism of Chemiluminescence: The conventional mechanism of diaryloxalate chemiluminescence was described in the previous report,[18] although the true mechanisms of chemiluminescence are not clearly known because of their complexity. Here, we show them in a general form as follows:

$$A + B \xrightarrow[\phi_{\text{int}}]{} (X\text{---}Y)^{\#} \xrightarrow[\phi_{\text{exc}}]{} C^* + D \qquad (1)$$

(Main reaction: with fluorescent substance [F])

$$C^* + F \xrightarrow[\phi_{\text{Trans}}]{} C + F^* \qquad (2\text{-}1)$$

$$F^* \xrightarrow[\phi_{\text{Fluor}}]{} F + h\nu \quad \text{(fluorescence or phosphorescence)} \qquad (2\text{-}2)$$

(Side reactions: with fluorescent substance [F])

$$\text{[Internal quenching]} \quad F^* \rightarrow F + \text{heat} \qquad (3\text{-}1)$$

$$\text{[External quenching]} \quad F^* + Q \rightarrow F + Q \qquad (3\text{-}2)$$

In the present study, A is diaryloxalate (RO(COCO)OR) [A: bis(3,4,6-trichloro-2(pentyloxycarbonyl)phenyl)oxalate], B is hydrogen peroxide (H_2O_2), $(X\text{---}Y)^{\#}$ is a high energy intermediate [unknown], C^* is 1,2-dioxetane(excited state), C is carbon dioxide, D is phenol (ROH), F is fluorophore = 1-chloro-9,10-bis(phenylethynyl) anthracene, and Q means coexisting substances or by-products [quenchers].[17]

Overall chemiluminescent quantum yield, ϕ_{CL} is given by the equation:

$$\phi_{\text{CL}} = \phi_{\text{Exc}}\phi_{\text{Trans}}\phi_{\text{Fluor}} \text{ [with fluorescent substance],}$$

(where, $\phi_{\text{Exc}} = \phi_{\text{int}}\phi_{\text{exc}}$)[17,18].

Analysis. For the analysis of chemiluminescence characteristics, parameters such as apparent initial intensity (I_0') and apparent lifetime (τ'), were measured; relative initial intensity (I_r^0), relative lifetime (τ_r), and relative chemiluminescent energy (E_r) were determined using a chemiluminescence decay profile. Two approximation methods were employed. The symbol τ_r refers to a lifetime and they were determined by the following equations: $\tau = t/(\log_e I_0 - \log_e I)$ or $\tau = (t_2 - t_1)/(\log_e I_1 - \log_e I_2)$ where $I_0 = I(t = 0)$, $I = I(t = t)$, $I_1 = I(t = t_1)$, $I_2 = I(t = t_2)$; since $I(t) = I_0 \exp(-kt)$, i.e., $\log_e I = \log_e I_0 - kt$; $k = \tau^{-1}$, and $I\,(t = \tau) = (1/e)I_0$. In most cases, $\log_e I_2$ was taken as -5.0 for convenience in the first order approximation, since measurements were stopped at $\log_e I_2 = -5.0$, and $\log_e I_1 = \log_e I_0$ (at $t = 0$). I corresponds to the light intensity or CL energy in unit time and unit volume for the CL reagent. Apparent chemiluminescent energy E for the media was defined as $E = I_0\tau$, since $\int I'(t)\mathrm{d}t = I_0/k = I_0\tau$ has energy units, I_0 being measured in mW units and W is Joule·s^{-1} in SI units. The relative values of these parameters to those values of blank experiment were defined as follows: $I_r = (I/I_0^0)$, $\tau_r = (\tau/\tau_0)$, $E_r = (E/E_0)$, and the relative chemiluminescent energy (relative CL energy) will correspond to the relative luminescent quantum yield (ϕ_{rCL}). In the second approximation, it was assumed that the chemiluminescent intensity is composed of two components (main[I_1] and side reactions[I_2]).[18] Thus, intensity vs time decay profile is divided into two parts. That is, $I = I_1 + I_2$ (at any time), and $I_0 = I_{01} + I_{02}$ (at initial time); $I_1 = I_{01} \exp(-k_1 t)$, $I_2 = I_{02} \exp(-k_2 t)$, and $N_1 = N_{01} - 0.434\,k_1 t$, $N_2 = N_{02} - 0.434\,k_2 t$, since $N = \log_{10}(I/\text{mW})$. The relative initial intensities and lifetimes to those values of blank experiment were defined as follows: $I_{01}^{\,r} = I_{01}/I_0^0$, $I_{02}^{\,r} = I_{02}/I_0^0$ and $\tau_r = (\tau/\tau_0)$, where subscripts 1 and 2 denote the main and side reactions, respectively. Chemiluminescent energy (E) was defined as follows: $E = (I_{01}/k_1) + (I_{02}/k_2) = (I_{01}\cdot\tau_1) + (I_{02}\cdot\tau_2)$. $E_0 = (I^0_{01}\cdot\tau_{01}) + (I^0_{02}\cdot\tau_{02})$. Relative chemiluminescent energy, E_r was defined as follows: $E_r = (E/E_0)$ and it will also correspond to the relative overall chemiluminescent quantum yield (ϕ_{rCL}).

Results and Discussion

Dependence of Chemiluminescence on Thickness of Packed Powder. To examine the effect of thickness of packed powder on chemiluminescence, several kinds of packed powder with different thicknesses were prepared and measured. Results for silica and alumina powder as representatives of inorganic compounds are shown in Fig. 2a and b. As is seen in Fig. 2b, in the case of silica particles (type S-O), packed powder with 0.75 mm thickness shows higher chemiluminescent intensity than any other packed powder with greater than 1.5 mm thickness; in the range of 1.5 to 3 mm the CL intensities are not dependent on thickness. For alumina (type AX-25), similar thickness dependence is seen, although CL intensity attains a plateau in the range of 2.2 mm or more (Fig. 2a). This small difference in intensity profiles will be explained by the difference in wetting patterns of packed powders between alumina (pattern A) and silica (pattern B) as is shown in Fig. 3. Pattern B will be explained by the high absorption ability of silica. However, in both compounds, initial CL intensities (measured immediately after the injection of CL reagent was done; $t_1 = 60$ s) did not change irrespective of packed powder thickness. From the reproducibility point of view, relative measurement errors were small at any thickness. For example, RSD ($= 100\,(\triangle N/N)\%$) fell in the range of 1.6–

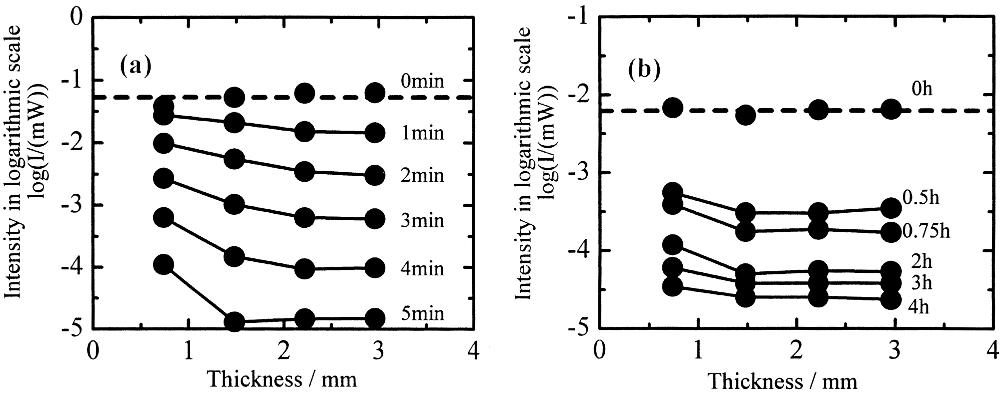


Fig. 2. The relationship between thickness of packed powder and chemiluminescent intensities at respective elapse of time for alumina (a) and silica (b).
Samples: alumina AX-25, silica S-O, Temperature: 25 °C, Relative humidity: 50 ± 3%, Water content in CL reagent: 100 ppm.

3.4% ($n = 5$) for alumina (AX-25) and 0.5 to 1.5% ($n = 5$) for silica (S-O) at the 1.5 mm thickness corresponding to one piece of aluminum plate. Thus, we have mainly used one piece of aluminum plate with 1.5 mm thickness in the present work.

Classification of Solid Media by the First Approximation Method. Around thirty kinds (ca., 90 samples) of inorganic solid media were examined through the chemiluminescent experiments. Using measured numeral values such as apparent chemiluminescent intensities and apparent lifetimes, relative initial intensities (I_r^0), relative lifetime (τ_r) and relative energies ($E_r = I_r^0\tau_r$) of chemiluminescence were determined, on the assumption that the chemiluminescence reactions are first-order chemical reactions, blank chemiluminescence being a standard, as was already stated in the analysis section for the first approximation. The results have been examined and selected. Among many sample materials measured, only favorable ones are cited in Table 1. That is, at least one of the three parameters of relatively estimated values (I_r^0, τ_r, or E_r) to those for the blank experiment, is greater than unity. As Table 1 shows, inorganic solid media were classified into several groups: (1) higher intensity and shorter lifetime group (G-1), (2) lower intensity and longer lifetime group (G-2), (3) higher intensity and longer lifetime group (G-3), (4) lower intensity and shorter lifetime group (G-4), and another group of (5) higher chemiluminescent energy group (G-5). We will discuss the characteristics of these groups in the following sections. Discussions were mainly based on the data of Table 1, which were obtained from the first-order approximation.

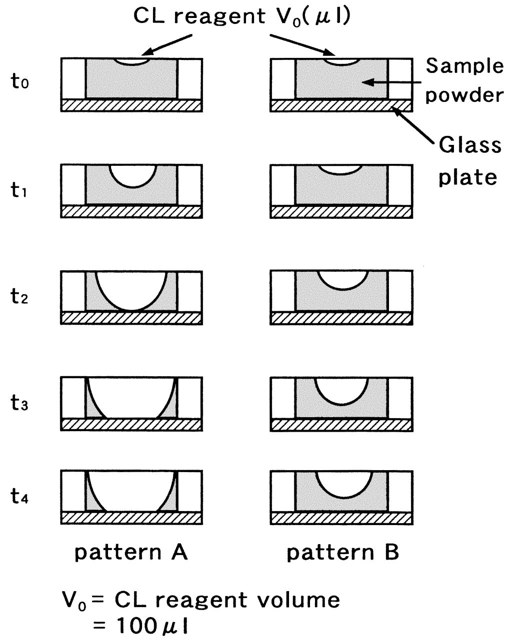


Fig. 3. Schematic drawing of typical wetting patterns of CL reagent.

Higher Intensities and Shorter Lifetime Group ($I_r^0 > 1$, $\tau_r < 1$): As shown in Table 1, many aluminum oxides and silicon oxides gave relatively high initial intensities. Other materials such as titanium dioxides (1010 type; $I_r^0 = 2.7$), zinc oxide [$I_r^0 = 3.4$], functional powders Sn/In_2O_3 [ITO; $I_r^0 = 1.9$], $SbSnO_2/TiO_2$ [W-1-P; $I_r^0 = 1.8$], hexagonal boron nitrides (h-BN) [GP; $I_r^0 = 2.3$, SP-1; $I_r^0 = 2.6$, SP-2; $I_r^0 = 2.5$], and a couple of calcium carbonates [3N-C; $I_r^0 = 1.5$, 3N-D; $I_r^0 = 1.1$], also belong to this group (G-1). Glass fiber filter (GC-50; $I_r^0 = 17.0$) and silica fiber filter (QR-100; $I_r^0 = 2.1$, [or $I_r^0 = 3.4$ when the filter surface was treated with ethanol]) were also measured here for comparison.[17] Glass fiber filter (GC-50) gave the highest initial intensity among the filters used in the previous study.[17] Ingredients of the glass fiber are approximately as follows: SiO_2 (62%), B_2O_3 (11%), Na_2O (10%), Al_2O_3 (6%), BaO (5%), K_2O (3%), and CaO (3%). In the present work, thirteen of fifteen aluminum oxides gave a higher intensity than blank CL (i.e., $I_r^0 = 1$); the highest one among them is alumina sphere particles the AX-25 (25 µm; $I_r^0 = 17.0$). This is comparable to the glass fiber filter (GC-50). AX-50 [$I_r^0 = 13.5$; $d = 50$ µm] gave a relative initial intensity of 13.5, and some particle size effect seems to exist. In this connection, alumina from another company (Wako Chemical Industry: Japan) [012-01965; $I_r^0 = 10.0$, $d = 75$ µm] was measured to compare the particle size effects. The tendency was found that the smaller the particle size, the higher the enhancement effects (d: 25–75 µm).

Aluminum hydroxides also gave relatively higher values, such as CW-375-HT [$I_r^0 = 10.7$; d (average diameter) = 66 µm; gibbsite], C-31 [$I_r^0 = 10.0$; $d = 50$ µm], CW-325-LV ($I_r^0 = 8.5$; $d = 27$ µm), C-315 ($I_r^0 = 7.8$; $d = 14$ µm). The purity

Table 1. Parameters on Chemiluminescence Characteristics for Inorganic Materials Which Were Obtained from an Intensity vs Time Profile Using a First Approximation Method*

Compounds	Relative Initial intensities	Relative Lifetimes	Relative Chemiluminescence Energies**
(Inorganic)	I_r^0	τ_r	E_r
blank	1.00[a)]	1.00[b)]	1.00[c)]
[Alumina: Al_2O_3] (spherical particles)			
AX-25 (25 μm)	17.0	1.20×10^{-2}	0.184
AX-50 (50 μm)	13.5	2.00×10^{-2}	0.264
{Wako 012-01965 (75 μm)}	10.0	2.36×10^{-2}	0.236
([low sodium] alumina)			
ALM-41-01 (2.3 μm)	2.24	8.80×10^{-2}	0.197
AL-41 (30–45 μm)	2.01	8.80×10^{-2}	0.441
([easy sintering] alumina)			
AES-11 (0.4 μm)	2.14	8.01×10^{-3}	1.71×10^{-2}
AES-12 (0.4 μm)	1.70	6.38×10^{-3}	1.08×10^{-2}
(aluminum hydroxides)			
C-301 (1.06 μm)	5.89	4.39×10^{-2}	0.259
C-308 (7.1 μm)	3.47	0.224	0.777
C-315 (14 μm)	7.76	8.40×10^{-2}	0.652
CW325LV (27 μm)	8.51	9.20×10^{-2}	0.783
C-31 (50 μm)	10.0	0.136	1.36
CW-375HT (66 μm)	10.7	0.152	1.62
[Glass fiber filter]			
GC-50	17.0	7.10×10^{-2}	1.21
{Silica fiber filter]			
QR-100	2.14 (3.39)[d)]	0.871 (1.17)[d)]	1.86 (3.97)[d)]
[Silica: SiO_2]			
S-O (3.0 μm)	3.24	0.536	1.74
SW-CO (20 μm)	2.95	1.52	4.48
S-CO (23 μm)	3.09	0.847	2.62
S-COL (28 μm)	2.57	0.707	1.82
Wako C-200 (75–150 μm)	2.24	1.05	2.35
[Titanium oxides]			
TiO_2 (amorphous) 1010 (1–8 μm)	2.69	4.39×10^{-2}	0.118
[Zinc oxide: ZnO] (20 nm)	3.39	1.20×10^{-3}	4.07×10^{-3}
[Functional fine particles]			
Sn/In_2O_3 [ITO]	1.91	1.07×10^{-3}	2.04×10^{-3}
$Sb{\cdot}SnO_2/TiO_2$			
W-1-P	1.82	1.72×10^{-3}	3.13×10^{-4}
[Ceramics]			
BN(boron nitride) (hexagonal system)			
SP-1 (0.6 μm)	2.63	1.29×10^{-2}	3.39×10^{-2}
SP-2 (0.8 μm)	2.45	5.77×10^{-3}	1.41×10^{-2}
GP (3.5 μm)	2.29	9.85×10^{-3}	2.26×10^{-2}
[Carbonate]			
($CaCO_3$)			
3N-B (0.5–1 μm)	0.55	1.53	0.843
3N-C (1–5 μm)	1.48	1.34	1.99
3N-D (> 5 μm)	1.10	2.23	2.44

*: Experimental life-time was determined using a simple linear line (first order reaction was assumed).

**: Chemiluminescent energy, E was defined as follows; $E = I_0\tau$, and it will be related to an apparent quantum yield.

a) $I_r^0 = (I_0/I_o^0)$; b) $\tau_r = (\tau/\tau_o) = (k_o/k)$; c) $E_r = (E/E_o)$, $E_0 = (I_0^0/k_0) = I_0^0\tau_0$

For blank CL, $I_o^0 = 2.20 \times 10^{-3}$ [mW]; $k_o = 3.02 \times 10^{-4}$ [s^{-1}]; $\tau_0 = 3300$ [s].

Where, I_0 means initial chemiluminescence intensity for respective solid media, and I_0^0 is for blank CL experiment, i.e., a (hole) slide glass was used as a solid media. Relative CL energy E_r will be correspondent to the relative CL quantum yield.

d) Values in parentheses were obtained from the use of a silica fiber filter with ethanol treatment

τ is experimentally determined by the use of the following equation;

$\tau = 0.4342\ (t_2 - t_1)/(\log_{10} I_1 - \log_{10} I_2)$ {First order reaction is assumed}.

since, $I = I_0 \exp[-kt]$, $\log_e I_1 = \log_e I_0 - k\, t_1$ --- (1),

$\log_e I_2 = \log_e I_0 - kt_2$ --- (2) , $\therefore k = (\log_e I_1 - \log_e I_2)/(t_2 - t_1) = \tau^{-1}$

of the respective sample of aluminum hydroxide series is more than 99.8%. Taking into account the fact that CW-325LV [$I_r^0 = 8.5$; $d = 27$ μm] has the highest purity (99.9%), we find that the main difference among the series is particle size. Therefore, varying particle size will have a strong effect on chemiluminescence characteristics. This series also has particle size effects. The larger the particle size, the stronger the intensity ($d = 14$–66 μm). But C-308 [$I_r^0 = 3.5$; $d = 7.1$ μm, water content = 0.07%] and C-301 [$I_r^0 = 5.9$; $d = 1.1$ μm, water content = 0.16%] showed a different tendency to this simple rule. Compared with the small amount of constituents or physical properties in both samples, differences in water content may be responsible for the small intensity enhancement.

On the other hand, extra high purity alumina (more than 99.99%), (AKP-30 [$I_r^0 = 0.51$; $d = 0.39$ μm], AKP-50 [$I_r^0 = 0.78$; $d = 0.10$–0.3 μm]) showed relatively low intensity compared with other alumina for solid surface chemiluminescence. In this case, both alumina were completely crystalline state (α-alumina), and thus they lost their catalytic activities. Alumina has a variety of species, such as high temperature type (1100 °C) crystal (α-alumina), crystal alumina hydrate, and several metamorphoses (γ-group: γ, ρ, χ, η, δ, κ, θ type etc.), and amorphous alumina.[20] Particle surfaces of alumina other than α-alumina have been considered to have strong activities.[19] However, XRD patterns of AX-25, and AX-50 also showed crystalline form of α-alumina, but nevertheless they exhibited strong luminescence intensities. Detailed analysis of XRD patterns taught us that they also have other crystalline forms such as γ alumina (η, δ, and θ). If we consider these facts, in the cases of solid substances as for chemiluminescent media, it will be essential to take into account the crystal forms, i.e., activities of surfaces of solid media other than chemical constituents. After all, we have to consider that for inorganic solid media, crystal forms, degree of crystallinity including amorphous state, particle sizes, contents of combined or adsorption water, and other factors (such as lattice defects, electronic structures, chemical compositions) will affect the surface activities of solid media on chemiluminescence.

Silica particle series, S-O [$I_r^0 = 3.2$; $d = 3.0$ μm], SW-CO [$I_r^0 = 3.0$; $d = 20$ μm], S-CO [$I_r^0 = 3.1$; $d = 23$ μm], S-COL [$I_r^0 = 2.6$; $d = 28$ μm] which were obtained from the same company), and other silica (C-200 [$I_r^0 = 2.2$; $d = 7$–150 μm] from Wako Chemicals, JAPAN) show a fairly clear relationship between relative chemiluminescent intensities and particle sizes, i.e., the smaller the particle size, the higher the initial intensities (3–150 μm), although the particle size dependences are not so strong. These values show that the effects of initial intensity enhancement for silica are somewhat higher than that of silica fiber filter (QR-100) without surface treatment, and this relatively small difference will be due to the difference in surface area or surface neighborhood geometries (or surface characteristics).

The main constituents of the glass fiber filter (GC-50) are SiO_2, B_2O_3, Na_2O, Al_2O_3, BaO, CaO and K_2O in the order of contents as stated already. From the results of preparatory experiments for each constituent (used as oxide) as solid media, SiO_2 and Al_2O_3 are considered to be the most effective constituents among them for chemiluminescence enhancement, although Na_2O (or NaOH) will have possibility of strong CL effect from the preliminary experiment. Considering the similarity of intensities of silica fiber filter (QR-100; $I_r^0 = 2.1$, [$I_r^0 = 3.4$ surface treated]) and silica powder ($I_r^0 = 2.2$–3.2) on solid surface chemiluminescence, alumina will be the most effective component among glass fiber constituents to the initial intensity enhancement of chemiluminescence.

Of three spherical titanium dioxides, only type 1010 ($I_r^0 = 2.69$, $d = 1$–8 μm) gave the relative intensity of greater than unity. Although both 0510 ($I_r^0 = 0.68$) or 0511 ($I_r^0 = 0.054$) types of titanium dioxides have small particle size (distribution) of $d = 0.2$–1.0 μm, relative intensity I_r^0 is less than 1, and especially 0511 has very low value. The reason for this is that 0511 type of TiO_2 is mixed crystals of both anatase- and rutile-types, while the other two are amorphous. Type 1010 has a rather greater particle size distribution (1–8 μm), and this suggests that for chemiluminescent enhancement amorphous state and particles with appropriate sizes are preferable, like the alumina and silica gel series shown above.

Lower Intensities and Longer Lifetime Group ($I_r^0 < 1$, $\tau_r > 1$): Substances belonging to this group are rare; only one compound corresponds to this group (G-2), that is, a kind of ultra pure calcium carbonate, 3N-B [$I_r^0 = 0.55$; $\tau_r = 1.53$; $d = 0.5$–1.0 μm]. Calcium carbonates (3N series; 99.9%+) also show the following particle size dependence on chemiluminescence: 3N-A [$I_r^0 = 0.17$; $d < 0.5$ μm], 3N-B [$I_r^0 = 0.55$; $d = 0.5$–1.0 μm], 3N-C [$I_r^0 = 1.48$; $d = 1.0$–5 μm], 3N-D [$I_r^0 = 1.10$; $d > 5$ μm]. As shown in the previous paper,[18] if chemiluminescent quantum yield is maintained constant, the luminescent energy must be constant ($E_r = I_r^0\tau_r = E_r^0 = 1 \times 1 = 1$). Thus, when reaction rate(k) increases, lifetime (τ_r) will decrease (i.e., $I_r^0 > 1$, $\tau_r < 1$). However there are a very few cases of examples with opposite directions ($I_r^0 < 1$, $\tau_r > 1$) as shown in Table 1. In the present case, luminescent energy is $E_r = I_r \cdot \tau_r = 0.84$ and nearly unity.

Higher Intensities and Longer Lifetime Group ($I_r^0 > 1$, $\tau_r > 1$): This group has apparently greater energy than that of blank CL, i.e., $E_r = I_r^0 \cdot \tau_r > 1$ ($= E_r^0 = E_0/E_0$: relative luminescent energy for blank), and this phenomenon can only be explained if luminescence quantum yield is not constant (increased quantum yield should be assumed). A few substances belong to this group, such as several silica and high purity calcium carbonates.

For silica, SW-CO [$I_r^0 = 2.95$, $\tau_r = 1.52$, $E_r = 4.48$; $d = 20$ μm] and Wako gel C-200 [$I_r^0 = 2.24$, $\tau_r = 1.05$, $E_r = 2.35$; $d = 75$–150 μm] correspond to this group. For high purity calcium carbonate, two of four samples, i.e., 3N-C [$I_r^0 = 1.48$, $\tau_r = 1.34$, $E_r = 1.99$; $d = 1$–5 μm] and 3N-D [$I_r^0 = 1.10$, $\tau_r = 2.23$, $E_r = 2.44$; $d > 5$ μm] correspond to this group, although these values were obtained for the first-order approximation.

Lower Intensities and Shorter Lifetime Group ($I_r^0 < 1$, $\tau_r < 1$): All other substances that do not belong to the above three groups correspond to this group (G-4), and they seem to be useless from the chemiluminescence applications point of view.

Higher Energy Group than Blank ($E_r = I_r^0 \cdot \tau_r > 1$): All materials that belong to the group of ($I_r^0 > 1$, $\tau_r > 1$: G-3), naturally correspond to this group (G-5), and in the first group, a few aluminum hydroxides series C-31 [$I_r^0 = 10.0$, $\tau_r = 0.136$, $E_r = 1.36$; $d = 50$ μm], and CW-375-HT [$I_r^0 = 10.7$, τ_r

= 0.152, E_r = 1.62; d = 66 μm], and most silica gel group S-O [I_r^0 = 3.24, τ_r = 0.54, E_r = 1.74; d = 3.0 μm], S-CO [I_r^0 = 3.09, τ_r = 0.85, E_r = 2.62; d = 23 μm], and S-COL [I_r^0 = 2.57, τ_r = 0.71, E_r = 1.82; d = 28 μm] correspond to this group. Furthermore, the glass fiber filter GC-50 [I_r^0 = 17.0, τ_r = 0.071, E_r = 1.21], and the silica fiber filter QR-100 [I_r^0 = 2.14 (3.39), τ_r = 0.87 (1.17), E_r = 1.86 (3.97)] also correspond to this group. The values in parentheses were obtained when solid surface treatment by ethanol was carried out. In the second group (G-2), there are no corresponding substances.

Classification of Solid Media with Higher (Second) Approximation. In the previous paper, chemiluminescent parameters such as relative initial intensities (I_r^0), relative lifetime (τ_r), and relative luminescent energies (E_r) for organic polymers were determined.[18] Calculations were done by assuming the chemiluminescent reactions to be quasi first order reactions. However, some solids did not obey this assumption, i.e., there were several substances that gave apparent chemiluminescent energies higher than unity ($E_r = I_r^0\tau_r > 1$). In that case, we considered that the chemiluminescent reactions were expressed by the sum of main reaction and side-reactions, and the intensity (I) vs time (t) profile ($I = I(t)$) was divided into two corresponding parts ($I = I_1(t) + I_2(t)$). Using this conception, or second (higher) approximation, almost all polymer substances used in the previous study, were reasonably explained, except for a few substances.[18]

For inorganic substances used in the present work, there were nine substances that had greater relative luminescent energies (E_r) than E_r = 1.5, and similar calculations to those for polymer compounds were carried out. The results are shown in Table 2. Due to these treatments, relative energies of most inorganic solid substances fell into a value of around one: For example, the relative energy for CW-375HT (aluminum hydroxide) became; 1.62 [first approximation] → 1.04 [second approximation]; S-COL(silica gel) 1.82 → 0.61; S-CO(silica-gel) 2.62 → 0.82 ; S-O(silica gel) 1.74 → 0.61; Wako C-200(silica gel) 2.35 → 1.16; 3N-C($CaCO_3$) 1.99 → 1.31; 3N-D ($CaCO_3$) 2.44 → 1.59. However, even after this treatment (second order approximation) was carried out, several special solids exhibited greater relative luminescent energies than E_r = 1.5, such as SW-CO(silica gel) 4.48 → 2.42; 3N-D($CaCO_3$) 2.44 → 1.59; QR-100 (silica fiber filter)[17] which was previously studied was again measured for comparison, and this time the silica fiber filter was treated with ethanol to raise the reproducibility. Due to this treatment, initial intensity and lifetime for QR-100 increased at the same time. After division of intensity vs time profile for QR-100, it still gave the highest relative energy among the ninety samples, although it was reduced from 3.97 to 3.41.

Selected Inorganic Solid Media. Among around ninety powdered samples, excellent data were selected. Spherical particles, AX-25 (I_r^0 = 17.0, τ_r = 0.012, E_r = 0.18; d = 25 μm) gave the highest intensity enhancement, and high purity calcium carbonate, 3N-D (I_r^0 = 1.10, τ_r = 2.23, E_r = 2.44; $d >$ 5 μm) gave the longest lifetime increase. SW-CO(silica gel) gave the highest energy increase by the first order approximation [I_r^0 = 2.95, τ_r = 1.52, E_r = 4.48; d = 20 μm]. But the energy of SW-CO decreased by the second approximation [E_r = 4.48 (1st) → E_r = 2.42 (2nd)].

Treated silica fiber filter (QR-100) gave the highest chemiluminescent energy among solid media after the second approximation [E_r = 3.97 (1st) → E_r = 3.41(2nd)].

For all of these representative and related substances, intensities vs time profiles are given in Fig. 4. Generally, it might be said that solids with high initial intensities tend to show a linear relationship between $\log_{10}$ (I/mW) vs time plots. In the next section, the reasons why some solid media will give higher intensities or higher energies than blank values are discussed.

Catalytic Activities and Change of Quantum Yields on Solid Surface Enhancements. As stated above, we have shown the existence of enhancement phenomena for chemiluminescence intensities and the increase in chemiluminescent energies using inorganic solid media. This will be partially explained for these phenomena by introducing two key phrases: *catalytic activity* and *change in quantum yield*. Classification of solid media stated above (G-1–G-5) will be explained by the two categories or combinations of key phrases;

(1) *catalytic activity + constant quantum yield*, and (2) *catalytic activity + change (increase or decrease) in quantum yield.*

Catalytic reactions usually cause increase in reaction rates, and solid media that behave like positive catalysts bring chemiluminescence enhancement effects in intensities and shortening of lifetime. On the other hand, the converse is true for negative catalysts, i.e., they cause decrease in reaction rate and brings the reduction of intensities and elongation of lifetime, although this last case is rarely seen. These catalytic effects will be due to strain, surface potential, surface tension, micro pores, activation points, functional groups, polarity, lattice defects, changes in transition (activation) states of atoms or molecules, ions, or electronic states, etc. of media solids from a macroscopic or mesoscopic point of view. Here, quantum yield is assumed to be constant (microscopic point of view).

Increase in chemiluminescent quantum yields (ϕ_{CL}), (i.e., $\phi_{CL} = \phi_{Exc}\phi_{Trans}\phi_{Fluor}$) will cause increase in chemiluminescent energies, intensities and/or lifetime. These increases of quantum yields will be due to the inhibition of side reactions. For example, increase in ϕ_{Exc} will be obtained by the protection and/or stabilization of intermediates, and will bring the enhancement of luminescence. Another possible reason is increase in production efficiencies of excited molecules, that is, inhibitions of thermal decomposition of 1,2-dioxetane (C^*) and fluorophore (F^*) increase in ϕ_{Trans} and ϕ_{Fluor}. In the case of fireflies (*Luciola cruciata* etc.), it is considered that they bring the specific reaction field of narrow environmental space (i.e., luciferase, a kind of enzyme) to give the highest luminescent efficiency of ca. 90% with the fewest side reactions.[21] In special solid media, for quantum yield increase there might be some specific environment such as specific surface conditions or inner porous structures (pore size, form, crystallinity, morphorlogy, or lattice defects etc.). Finally, the mutual relationship among chemiluminescent parameters such as relative-chemiluminescent intensities (I_r^0), lifetime (τ_r), chemiluminescent energies (E_r), and catalytic activities and relative quantum yields (ϕ_r) are shown in Table 3.

In the near future, we will apply these solid surface en-

Table 2. Parameters on Chemiluminescence Characteristics for Representative Inorganic Materials, Which Were Obtained from Intensity vs Time Profile Using a Second (Higher) Approximation Method*

Inorganic Compounds	Relative Initial intensities^a) (I_{01r}; I_{02r})	Relative Life-times^b) (t_{1r}; t_{2r})	Relative Chemiluminescence Energies^c) (E_r)
blank^d)	(0.70; 0.30)	(0.72; 1.25)	(1.00)
[Al(OH)$_3$]			
C-31	(10.0; —)	(0.14; —)	1.56 (1 step)
CW-375HT	(10.0; 0.67)	(7.8×10^{-2}; 0.22)	1.04
Al$_2$O$_3$			
AX-25	(17.0; —)	(1.2×10^{-2}; —)	0.20 (1 step)
AX-50	(13.5; —)	(2.0×10^{-2}; —)	0.30 (1 step)
[Glass fiber filter]			
GC-50	(17.0; —)	(7.0×10^{-2}; —)	1.35 (1 step)
[SiO$_2$]			
S-COL	(2.51; 5.65×10^{-2})	(0.17; 2.15)	0.61
S-CO	(3.08; 7.60×10^{-2})	(0.17; 2.95)	0.82
S-O	(3.12; 0.12)	(0.13; 1.21)	0.61
SW-CO	(2.52; 0.42)	(0.51; 2.13)	2.42
Wako C200	(1.35; 0.90)	(0.07; 1.03)	1.16
[Silica fiber filter]			
QR-100^e)	(3.27; 0.12)	(0.85; 2.35)	3.41
[CaCO$_3$]			
3N-C	(1.20; 0.28)	(0.50; 2.04)	1.31
3N-D	(0.56; 0.54)	(0.34; 2.29)	1.59

*: It was assumed that the intensity vs lifetime profile is composed of two components, which are corresponding to main and side reactions. Thus, it was divided into two parts. That is, $I = I_1 + I_2$ and $I_0 = I_{01} + I_{02}$; $I_1 = I_{01} \exp(-k_1 t)$, $I_2 = I_{02} \exp(-k_2 t)$; i.e., $\log_{10}(I_1) = \log_{10}(I_{01}) - 0.434\, k_1 t$, $\log_{10}(I_2) = \log_{10}(I_{02}) - 0.434\, k_2 t$.

**: Not divided here, since the first approximation fits well.

a) $I_{01r} = I_{01}/I_0^0$, $I_{02r} = I_{02}/I_0^0$ (For blank CL, $I_0^0 = 2.20 \times 10^{-3}$ mW [first approx.], and $I_{01}^0 = 1.37 \times 10^{-3}$ mW, $I_{02}^0 = 0.83 \times 10^{-3}$ mW [second approx.])

b) Determined for main (τ_1) and side (τ_2) reactions. $\tau_{1r} = \tau_1/\tau_0$, $\tau_{2r} = \tau_2/\tau_0$ (For blank CL, $\tau_0 = 3300$ (s) [first approximation.], and $\tau_{01} = 2370$ (s), $\tau_{02} = 4110$ (s) [second approximation]

c) Chemiluminescent energy, E was defined as follows; $E = (I_{01}/k_1) + (I_{02}/k_2) = I_{01}\cdot\tau_1 + I_{02}\cdot\tau_2$. Relative energies, $E_r = (E/E_0)$ will be correspondent to the relative CL quantum yield.; where $E_0 = I_{01}^0\cdot\tau_{01} + I_{02}^0\cdot\tau_{20}$.

d) This time, relative parameters were obtained as the ratio of sample parameter (obtained from the second approximation) to a blank one (obtained from the first approximation) for convenience as shown in a) and b).

e) Values used were obtained from the samples with ethanol treatment.

hancement effects to the high sensitive sensor of instrumental analyses such as HPLC.

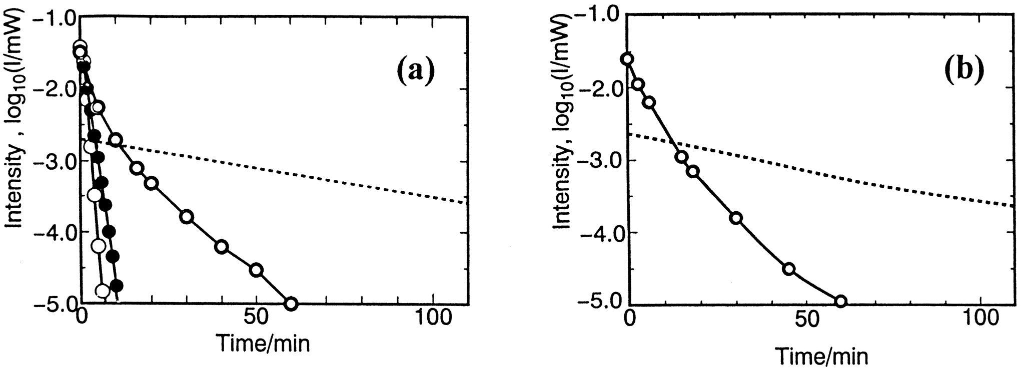
Many inorganic substances have been examined to find the influence of solid media on chemiluminescence. The effects of solid media were classified into four or five groups that characterize the chemiluminescence characteristics using three kinds of parameters. That is, relative initial intensity (I_r^0), relative lifetime (τ_r), and relative luminescent energy (E_r) were used when blank chemiluminescence were used as the standard for comparison (I_0^0, τ_0, and E_0). Parameters are obtained from the first approximation (assumed as first-order chemical reaction), or second approximation (it is considered that intensity vs time profile are composed of first-order main reaction and first-order side reactions). We adopted the second approximation only when relative luminescent energy exceeded 1.5 (i.e., $E_r > 1.5$) in the first approximation. Those groups thus obtained are as follows (due to first approximation):

(1) *Higher intensities and shorter lifetime group ($I_r^0 > 1$, $\tau_r < 1$):*

(Low sodium) alumina(AL-41, ALM-41-01), aluminum hydroxide(C-31, C301, C-308, C-315, CW375-HT, CW-325-LV), spherical alumina particles(AX-25, AX-50), Wako alumina(012-01965)

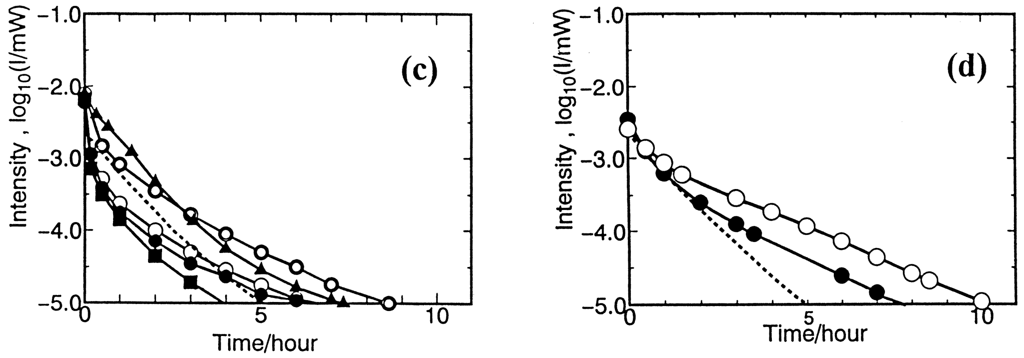
(2) *Lower intensities and longer lifetime group ($I_r^0 < 1$, $\tau_r > 1$):*

High purity calcium carbonate (3N-B)



Solid media: alumina spherical particles (AX-25, AX-50) and a glass fiber filter (GC-50)
○: AX-25, ●: AX-50, ◎: GC-50 ----: Blank

Solid media: aluminum hydroxide
○: CW-375HT, ----: Blank



Solid media: silica spherical particles (SW-CO, S-CO, S-COL, S-O) and a silica fiber filter(QR-100)
◎: SW-CO, ○: S-CO, ●: S-COL, ■: S-O, ▲: QR-100, ---- : Blank

Solid media: ultra pure calcium carbonates
○: 3N-D, ●: 3N-C, ----: Blank

Fig. 4. The relationship between luminescent relative intensities and time for representative solid media on solid surface chemiluminescence (Measured at 25.1 °C, Relative humidity: 50–53%).
(a) Solid media: alumina spherical particles (AX-25, AX-50) and a glass fiber filter (GC-50). ○: AX-25, ●: AX-50, ◎: GC-50, ----: Blank.
(b) Solid media: aluminum hydroxide, ○: CW-375HT, ----: Blank.
(c) Solid media: silica spherical particles (SW-CO, S-CO, S-COL, S-O) and a silicafiber filter (QR-100), ◎:SW-CO, ○: S-CO, ●: S-COL, ■: S-O, ▲: QR-100, ----:Blank.
(d) Solid media: ultra pure calcium carbonates, ○: 3N-D, ●: 3N-C, ----: Blank.

(3) *Higher intensities and longer lifetime group ($I_r^0 > 1$, $\tau_r > 1$):*

Spherical silica particles (SW-CO), silica fiber filter (QR-100), high purity calcium carbonate (3N-D)

(4) *Lower intensities and shorter lifetime group ($I_r^0 < 1$, $\tau_r < 1$):*

All materials that do not belong to (1)–(3) groups among ninety samples.

(5) *Higher energy group than blank luminescence ($E_r = I_r^0 \tau_r > 1$:*

All substances in (3) and substances in no other group correspond to this group. SW-CO, QR-100, 3N-D.

Among the above substances, alumina spherical particles (AX-25) and a glass fiber filter (GC-50) gave the highest intensity enhancement (ca. $I_r^0 = 17$ times), and a high purity calcium carbonate (3N-D) gave the longest lifetime (ca. $\tau_r = 2.2$ times: first approximation), although a silica fiber filter (QR-100) and a silica gel (SW-CO) also gave the same longer lifetime (second approximation). From a chemiluminescent energy point of view, a silica fiber filter (QR-100) and silica gel (SW-CO) gave the highest relative energies of 2–2.3 times.

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Table 3. Mutual Relationship among Chemiluminescent Parameters, (such as relative chemiluminescent Intensities (I_r^0), Relative Lifetime (τ_r), Relative Chemiluminescent Energies (E_r))* vs Catalytic Activities (θ), and Relative Quantum Yields (φ_r)

Relative quantum yields (φ_r)	Catalytic activities (θ)		
	Negative	None	Positive
$0 < \varphi_r$	(a)** (① G-2; ③ G-3; G-5) ① $0 < I_r^0 < 1$, $1 < \tau_r$, $(1 < E_r)$ ② $I_r^0 = 1$ $1 < \tau_r$, $(1 < E_r)$ ③ $1 < I_r^0$ $1 < \tau_r$, $(1 < E_r)$	(b)** (G-5) $1 < I_r^0$ $\tau_r = 1$ $(1 < E_r)$	(c)** (G-5) $1 < I_r^0$ $0 < \tau_r < 1$ $(1 < E_r)$
$\varphi_r = 1$	(d)** (G-2) $0 < I_r^0 < 1$ $1 < \tau_r$ $(E_r = 1)$	(e)** (blank) $I_r^0 = 1$ $\tau_r = 1$ $(E_r = 1)$	(f)** (G-1) $1 < I_r^0$ $0 < \tau_r < 1$ $(E_r = 1)$
$0 < \varphi_r < 1$	(g)** (G-2) $0 < I_r^0 < 1$ $1 < \tau_r$ $(0 < E_r < 1)$	(h)** ($\fallingdotseq$ G-2) $0 < I_r^0 < 1$ $\tau_r = 1$ $(0 < E_r < 1)$	(i)** (① G-4; ③ G-1) ① $0 < I_r^0 < 1$, $0 < \tau_r < 1$, $(0 < E_r < 1)$ ② $I_r^0 = 1$, $0 < \tau_r < 1$, $(0 < E_r < 1)$ ③ $1 < I_r$, $0 < \tau_r < 1$, $(0 < E_r < 1)$

*: Where chemiluminescent energy (E_r) is conveniently defined as $E_r = I_r^0\tau_r$

**: (a), (b), …, and (i) represent blocks generated by the possible combinations of relative quantum yields (φ_r) and catalytic activities (θ). Relative quantum yield (φ_r) is considered to correspond to relative chemiluminescent energy (E_r) from the definition of quantum yield, and catalytic activities (θ) will be corresponding to k (rate constant, and reverse of τ_r) as far as the chemiluminescent energy (E_r) is constant [i.e.: $\theta_r \propto k \propto I_r^0/E_r$]. ①–③ show possible combinations of I_r^0, τ_r, and E_r, ; for example, in block (a) [with $\varphi_r > 1$, θ_r negative], the enequalities $1 < \tau_r$ and $1 < E_r$ seems reasonable. However, I_r^0 have three possible values (regions) under the restriction of $E_r = I_r^0\tau_r$, and ① correspond to G-2; ③ correspond to G-3 and G-5.

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